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THE INTRINSIC VISCOSITY OF LOW MOLECULAR WEIGHT POLYSTYRENES.

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The relation between intrinsic viscosity, $[\eta]$, and number average molecular weight, M, has many times been investigated (1–13) for polystyrenes of high molecular weight, usually in the region 50,000–500,000, though recently this range has been extended down to 3,000 (13) and up to 1,800,000 (7, 11). It is of interest to explore this relation for very low molecular weight polymers, to ascertain whether the Mark-Houwink relation $[\eta] = K.M^{a}$., which describes high polymers, continues to hold down to very short chain lengths with the same values of K and a or whether, for low polymers, $a=1$ (Staudinger relation), as is sometimes assumed. Moreover, if a single relation does hold over the whole range of molecular weights, then extension of the range investigated increases the reliability of determination of K and a. Indeed, extension of the range appears to be the only way of obtaining reliable values of these parameters. Experimental difficulties in molecular weight measurement, and in obtaining polymer samples of exactly comparable molecular weight distribution, have so far prevented any two investigators from obtaining the same numerical values for the constants. The values found by different authors have been reviewed in a recent paper by Bawn, Freeman, and Kamaliddin (11).

In this work the author has prepared a range of polystyrenes of molecular weight 1,000–10,000 by catalysis by stannic chloride in solution in ethylene dichloride, and measured their number average molecular weight (cryoscopically in cyclohexane) and intrinsic viscosity in benzene and in cyclohexane at 25°C. The results are compared with previous determinations in similar molecular weight regions (14, 15) and with recent results (7–13) covering a much wider range.

Preparation of Polymer Samples.

The polystyrenes studied were all prepared at the same initial concentration of styrene (1.68 mole/litre) and stannic chloride (9.6×10^{-3} mole/litre) in solution in ethylene dichloride. Polymerisation was allowed to go almost to completion (80–90%); the reaction was then stopped by the addition of methyl alcohol, and

the polymer isolated by removal of the solvents and any remaining monomer by steam distillation. The dried polymer was then dissolved in benzene or cyclohexane, filtered to remove insoluble residues from the hydrolysed catalyst, freed from solvent by a further steam distillation and dried in a vacuum desiccator. Steam distillation was found to be a much more rapid and effective way of removing low boiling solvents than the more usual method of direct evaporation under vacuum, and has the advantage of leaving the polymer sample in a dry, brittle, porous form. If the solvents are merely pumped off at a pressure of approx. 10^{-2} mm. Hg., the polymer is left in a sticky, viscous, and finally in a glassy form, from which the last traces of solvent are almost impossible to remove, and which is very difficult to handle. A possible objection to the steam distillation is that further (thermal) polymerisation of any remaining monomer may occur. This possibility was tested experimentally, as described later, and found not to occur to any detectable extent.

By the above methods, a series of polymers of different average molecular weight was prepared by carrying out the reaction at different initial temperatures, varying from –20°C. to 80°C. Since the polymer samples were isolated completely by steam distillation, these samples have their full molecular weight distribution as determined by the reaction kinetics; partial fractionation, inevitable when polymers are isolated by precipitation, is avoided. In addition to these unfractionated polymers, a series of more homogeneous specimens was prepared by careful fractionation of a polymer prepared at 25° into 12 narrow fractions by precipitation from benzene solution by methyl alcohol. Details of this fractionation are given in a forthcoming paper (16) on the molecular weight distribution.

Materials and Methods.

Benzene used as solvent in the measurement of intrinsic viscosity was a " crystallisable " grade, further purified by shaking with concentrated sulphuric acid, washing with water, drying over $CaCl_2$ and P_2O_5, and distilling. Cyclohexane for the cryoscopic measurements was purified in the same way, and then subjected to exhaustive fractional crystallisations until the freezing point became constant at 6.505°C.

Since the cryoscopic method measures the *number* average molecular weight, it is very sensitive to the presence in the polymer of traces of low molecular weight impurities such as monomer or solvents. Such traces were found to be impossible to remove entirely by pumping at about 10^{-2} mm. Hg., or by one steam distillation. Effective purification was achieved by dissolving the steam distilled polymer in cryoscopic cyclohexane, and removal of the cyclohexane by further steam distillation Two such additions and removals of cyclohexane were always performed, and in some cases three. The effect of this treatment is that all other solvents are effectively carried off, and the only low molecular weight impurities remaining in the polymer are traces of cyclohexane, which do not affect the molecular weight determination in that solvent.

A possible objection to this method of purification is that the high temperature

of the steam distillation might affect the polymer molecular weight, either by depolymerisation (unlikely) or by further (thermal) polymerisation of traces of monomer. To test this objection, a polymer sample was subjected to repeated steam distillations, followed by addition of styrene monomer, and then by two further steam distillations, samples being isolated and molecular weights determined at each stage. The crude polymer was found to have a cryoscopic molecular weight of 3660, which was raised to 3950 by two steam distillations from cyclohexane, and unaffected by a further distillation or by the treatment with styrene and further distillations.

The number average molecular weights were calculated using the value of the cryoscopic constant for cyclohexane quoted in the International Critical Tables: i.e. $M=20150.\ w/\triangle T$ where $\triangle T$. is the depression of the freezing point in degrees Centigrade at a concentration of w grams polymer per gram cyclohexane. Measurements of $\triangle T$ were made for at least three different concentrations, and the limiting value of $\triangle T/w$ obtained by extrapolation to zero concentration. The accuracy of the molecular weights so obtained was usually $\mp$ 2%, but in some cases (referred to later) limited data made extrapolation uncertain to $\mp$ 5%.

The intrinsic viscosities were measured in benzene, and in some cases in cyclohexane, at 25°C. in a standard Ostwald viscometer with negligible kinetic energy correction (tested). All viscosities quoted are strictly kinematic viscosities, the densities of the polymer solutions not being measured, since they were always close to the density of the pure solvent and on extrapolation to zero concentration, identical. Concentrations are expressed in grams polymer per 100 c.c. solution, since these units are now used more widely than the earlier units, base moles per litre. Values of the reduced viscosity (η_{sp}/c) were determined on at least three different concentrations for each sample. Even with the low molecular weight polymers examined in this work, the reduced viscosity was found to vary appreciably with concentration and the value of the intrinsic viscosity $[\eta]$ was always determined by extrapolation of η_{sp}/c to its limiting value at $c=O$. Such extrapolation is sometimes a rather uncertain process, since at low viscosities, where the flow time in the viscometer is only slightly greater than that of the pure solvent, small errors in the measurement of flow time may make large errors in the derived value of $\eta_{sp.}$ ($=\eta_r - 1$, where η_r=ratio of flow times for solution and solvent). This uncertainty can be greatly minimised by plotting

$$2.303\ \frac{\log\ \eta_r}{c} \quad \text{as well as} \quad \frac{\eta_{sp}}{c} \quad \text{against concentration on the same graph.}$$

One set of experimental data thus provides two different extrapolation functions, which are both approximately linear with concentration, and which must both converge to the same point at zero concentration. The uncertainty in the measurement of $[\eta]$ can by this means be reduced to less than 1%. The maximum variation in values of $[\eta]$ derived from different sets of observations on the same polymer sample was $\mp$ 2% and usually much less.

Results.

Fig. 1 shows the results of cryoscopic measurements on the unfractionated polymers in cyclohexane, expressed as a plot of freezing point depression per unit concentration ($\triangle T/w$) against concentration (w) in grams polymer per gram cyclo-

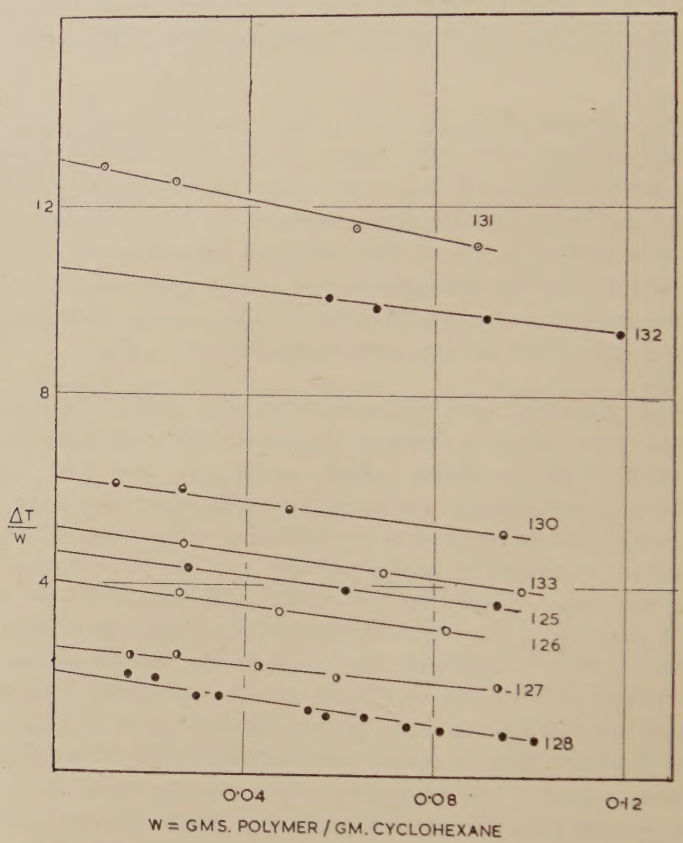

Fig. 1.—Cryoscopic Measurements on Unfractionated Polymers.

hexane. It can be seen that $\triangle T/w$ falls approximately linearly with concentration, and hence values of the number average molecular weight (M) were calculated from the limiting value $\lim_{w \to 0} \triangle T/w$

Fig. 2 shows some of the viscosity determinations in benzene solution, in order to indicate the degree of accuracy obtainable and to illustrate the value of the simultaneous plotting of $\frac{\eta_{sp}}{c}$ and $\frac{\log_e \eta_r}{c}$.

The values of M and $[\eta]$ for the unfractionated polymers and for the fractions, are collected in tables 1 and 2.

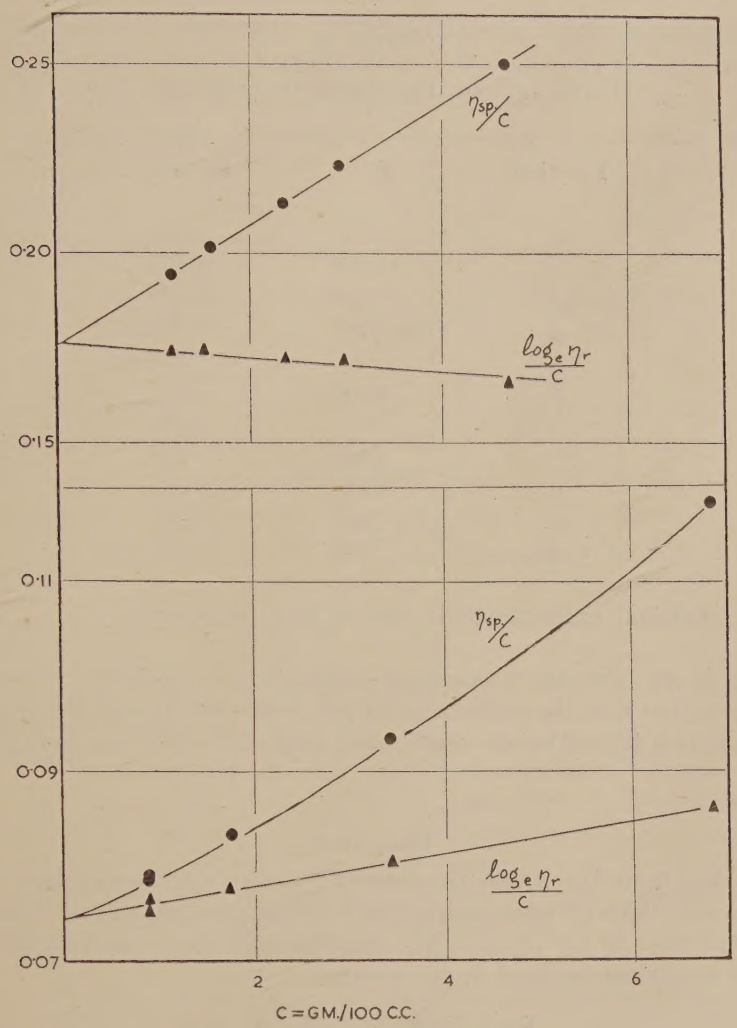

FIG. 2.—INTRINSIC VISCOSITY MEASUREMENTS.

$[\eta] = \lim_{c=0} \eta_{sp}/c.$

TABLE I.

MOLECULAR WEIGHT AND INTRINSIC VISCOSITIES FOR UNFRACTIONATED POLYMERS.

Sample No.	T°C. of polym.	M	$[\eta]$ Benzene	$[\eta]$ Cyclohexane
125	−31	4900	0.121	0.089
126	−27	5050	0.116	0.086
127	0	4100–4350	0.090	0.075
128	0	3950	0.088	0.075
133	16	3850	0.088	0.074
130	25	3250	0.075	0.064
132	78	1900	0.050	0.047
131	83	1550	0.048	0.047

TABLE 2.

M AND $[\eta]$ FOR FRACTIONS IN BENZENE.

Fraction	M.	$[\eta]$ Benzene
1	—	0.139
2	10,700	0.105
3	8,350	0.094
4	6800–7200	0.085
5	—	0.077
6	5,050	0.072
7	—	0.067
8	4,000	0.058
9	3,150	0.053
10	2800–3050	0.049
12	770	0.026

(Original unfractionated polymer had $[\eta]=0.076$).

It can be seen that the fractionated samples cover a fairly wide range of molecular weights, but that the unfractionated polymers, even though the temperatures of polymerisation differed by over 100°C. show only a three-fold variation in molecular weight.

Discussion.

It is clear from Fig. 2 that the reduced viscosity η_{sp}/c varies quite markedly with c, a result which is rather unexpected for these polymers of very low molecular weight. The slope of the η_{sp}/c—c line increases with increasing molecular weight, but not to the extent required by the equation

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c$$

which normally describes this concentration dependence for high polymers. If values of k' are calculated for the various polymers from $k' = \text{slope}/[\eta]^2$, it is found that k' decreases from a value of about 2 for the lowest polymers (M 1500) to an approximately constant value of about 0.4 for polymers of molecular weight greater than about 5000. The value of k' is usually found to be independent of molecular weight, and characteristic of a given polymer-solvent system, being high in a poor solvent and low in a good solvent. The explanation of the variation observed here in a single solvent may be that in the very lowest molecular weight polymers the chain is not long enough for it to assume the random configurations characteristic of true high polymers, and that only when its chain length exceeds about 50 monomer units does it approach true high polymer behaviour (for high molecular weight polystyrenes, the value of k' usually observed in benzene is 0.35 independent of molecular weight (17, 18).

In cyclohexane, the same trend of k' with molecular weight is observed, though it is less marked. The values of k' in cyclohexane are uniformly greater than those in benzene ,as would be expected in the poorer solvent.

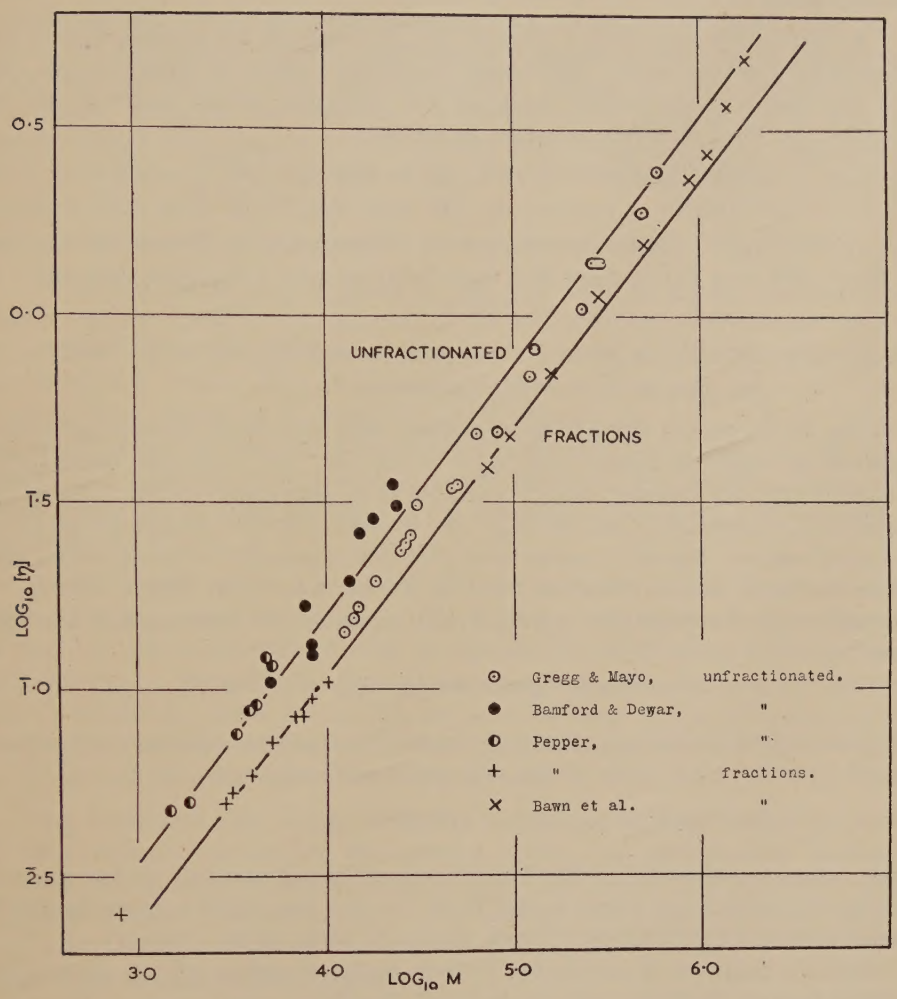

FIG. 3.—INTRINSIC VISCOSITY—MOLECULAR WEIGHT RELATION IN BENZENE.

The lines correspond to :—

$[\eta] = 4.37 \times 10^{-4} M^{0.66}$ (unfractionated polymers).
$[\eta] = 2.7 \times 10^{-4} M^{0.66}$ (fractions)

The recent measurements by Bawn (12, 18, 19), of k' and a for polystyrene in different solvents, indicate that these two constants are related ; in a good solvent k' is low and a high, and vice versa. The variation of k' with molecular weight observed here might, therefore, lead us to expect a related variation of a—i.e. that

a plot of log $[\eta]$ against log M would not be a straight line, but a curve of slope (a) increasing with molecular weight at any rate up to molecular weights of about 5,000. However, the observations recorded in Tables 1 and 2 and plotted in Fig. 3 reveal no such trend.

As can be seen from Fig. 3, plots of $\log_{10}[\eta]$—$\log_{10}$ M are straight lines of slope appreciably less than unity. The simple Staudinger relation is, therefore, not valid, and the results of the present work on low molecular weight polymers are best described by Mark-Houwink relations as follows :—

Unfractionated polymers $[\eta] = 2.27 \times 10^{-4}\ M^{0.72}$ .... (1)

Fractions $[\eta] = 4.17 \times 10^{-4}\ M^{0.60}$ .... (2)

The values of $[\eta]$ in cyclohexane solution for unfractionated polymers are not shown in Fig. 3, but they too conform to a linear relation with a slope less than one : viz.

$[\eta]$cyclo $= 9.66 \times 10^{-4}\ M^{0.58}$ .... (3)

the intrinsic viscosities in benzene and cyclohexane being related as follows

log $[\eta]$cyclo $=$ 0.80 log $[\eta]$benzene—0.10.

The above results are not in agreement with the simple Staudinger relation obtained by Kemp & Peters* (14), $\eta_{sp}/c = 5.4 \times 10^{-5}$ M. However, these authors measured very few samples, did not extrapolate to zero concentration, and, in fact, obtained constancy of K only for their two highest molecular weight samples. The Houwink relation, therefore, seems more probable, especially as the equations given above are fairly close to those obtained by Bamford & Dewar (15) in toluene. By a combination of experiments and theoretical methods, the latter authors concluded that :—

For unfractionated polymers $[\eta] = 4.40 \times 10^{-4}\ M^{0.65}$ .... (4)

They also argued theoretically that both the fractionated and unfractionated polymers should have the same value of the exponent, and calculated :—

For fractions $[\eta] = 2.92 \times 10^{-4}\ M^{0.65}$ .... (5)

Their actual experimental results for unfractionated polymers are in fact described well by the relation (1) found in this work, but for theoretical reasons Bamford & Dewar preferred the equation (4) with the lower value of the exponent.

For the purposes of calculating M from measured values of $[\eta]$, there is little to those between these two sets of relations. For fractionated polymers Bamford & Dewar's equation gives effectively the same value of M as does the author's relation ; for unfractionated polymers the difference is little greater than the experimental error. However, we should not expect exact correspondence, since one relation refers to benzene and the other to toluene solutions. The question whether both fractions and unfractionated polymers should give the same value of a cannot be decided by the experimental evidence presented here, but it seems likely, in view of the later discussion, that they should.

* Kemp and Peters, and Bamford & Dewar's actual values of K have here been adjusted to convert their concentrations (base moles/litre) to the g./100 c.c. units used here.

A comparison with recently published results on high molecular weight polystyrenes is revealing. In Fig. 3 are plotted on the same graph the present results, those of Bamford and Dewar, a series obtained by Gregg and Mayo (10) for unfractionated polystyrenes of M 50,000–600,000, and the recent results of Bawn, Freeman, and Kamaliddin (11) for fractions extending over the molecular weight range 72,000–1,800,000. For purposes of strict comparison, it should be remembered that Bamford & Dewar's intrinsic viscosities were measured in toluene, all others being determined in benzene. However, the difference is not large, and is probably within the experimental scatter of Bamford & Dewar's points. Also, Gregg and Mayo's measurements of $[\eta]$ were made at 30°C., all others being at 25°C. It has been shown by Frith (20), however, that while η_{sp}/c may vary with temperature if polymer and solvent do not mix athermally, the extrapolated value $[\eta]$ is temperature independent.

From the distribution of points in Fig. 3 it could be argued that each set of results was self consistent but not comparable with the other sets, i.e. that the points lie on three almost parallel lines, of slope 0.71–0.73, but displaced from one another by an amount greater than experimental errors. If this is so, we would have to conclude that differences in molecular weight distribution of the different polymers are great enough to make strict comparison impossible, and a single $[\eta]$, M relation unrealisable from data of the present accuracy. However, the following considerations make it possible to allow for some of the differences and narrow the apparent discrepancy.

Bawn's results refer to closely fractionated polymers, and we should, therefore, expect that his points on the log $[\eta]$, log M plot would lie below and to the right of those for unfractionated polymers, as required by the Bamford & Dewar theory, and as found by the author for low molecular weight polymers. If the line describing Bawn's results be raised by an amount corresponding to the difference between fractionated and unfractionated polymers, then it lies among the points obtained by Gregg and Mayo for unfractionated polymers.

The lower molecular weight polymers in Gregg and Mayo's series are known to have suffered appreciable fractionation during the precipitation method of isolation, as the authors themselves point out. This means that their lower points should lie further to the left in Fig. 3. The amount their points should be displaced cannot be exactly calculated, but may be approximately estimated from the following data taken from their paper.

CCl_4/Styrene Ratio	$[\eta]$	M
0.94	0.155	14,400 (isolated by ppt.
1.05	(not measured)	10,500 (complete isolation)
1.05	,, ,,	10,700 ,, ,,
1.18	0.142	12,700 (isolated by ppt.)

It can be seen that the polymers isolated without any fractionation have molecular weight about 20% less than that of the precipitated polymer. If we estimate (from the value of the CCl_4/Styrene ratio) a value of $[\eta]=0.15$ for unfractionated polymer of molecular weight 10,600, we obtain a point on the log $[\eta]$, log M plot about half way between the Gregg and Mayo line and that of the author and Bamford and Dewar.

The author's polymers were prepared by Friedel Crafts initiation, which gives rise to different kinetics and, hence, molecular weight distribution different from that of radical polymers. None the less, they are included in consideration here since their molecular weights are very low, and hence the distribution cannot be very wide and is not likely to be very different from that of radical catalysed polymers of similar molecular weight. This conclusion is strengthened by the observation that these polymers fit the same $[\eta]$, M relation as Bamford and Dewar's radical catalysed polymers.

It would seem, then, that all the results in Fig. 3 may legitimately be considered together, and described by a single relation for all unfractionated polymers over the whole range. The straight line drawn on Fig. 3 through the points for unfractionated polymers corresponds to

$$[\eta]=4.37\times10^{-4}.\ M^{0.66} \quad .... \quad .... \quad (6)$$

In this equation the exponent has an appreciably lower value than those found by the separate authors over their more limited ranges of molecular weight, but it agrees well with that theoretically obtained by Bamford and Dewar.

For closely fractionated polymers, the data are more plentiful but not always strictly comparable. On Bamford and Dewar's theory we should expect that the relation for fractions should have the same exponent as that for unfractionated polymers. The line on Fig. 3 corresponding to

$$[\eta]=2.7\times10^{-4}.\ M^{0.66} \quad .... \quad .... \quad (7)$$

does, in fact, describe with fair accuracy both Bawn's results for high molecular weight fractions and the author's for low molecular weights, and is very similar to Bamford and Dewar's theoretical relation (5) for fractions. It also provides a satisfactory description (with the reservations stated) of the following sets of recent results.

Wales, Williams, Thompson and Ewart (9) for fractions of M.W. 44,000–400,000 in benzene, find values of α varying between 0.69 and 0.75. Their actual measurements, however, if plotted in Fig. 3, lie roughly parallel to the line representing equation (7), with $[\eta]$ values about 12% greater. Earlier work by Ewart, Tingey, and Wales (6) had led to a value of α of 0.783, but the detailed results are not published.

Bueche's (11) values of intrinsic viscosity in benzene of fractions in the molecular weight range 135-805,000 were measured at 38°C., and may not be strictly comparable with the other results considered here. By themselves, they are best fitted by an exponent of 0.85. His points, however, straddle the line on Fig. 3 representing equation (7), and four of his six results lie close to it.

Goldberg, Hohenstein, and Mark (7) have measured intrinsic viscosities in toluene of fractions of molecular weight 200,000–1,800,000, and find an exponent of 0.62. However, it is possible to recalculate their results so that they apply to benzene solutions by means of the equation given by Bawn *et al.*(12) relating intrinsic viscosities of similar fractions in benzene and toluene solutions. Their points are then found to lie over their whole range close to the line on Fig. 3 representing equation (7).

The very extensive results of Outer, Carr, and Zimm (13) for fractions of M.W. 2,460–1,770,000 in toluene and in butanone may be similarly recalculated to refer to benzene, giving

$$[\eta]\text{benzene} = 1.36 \times 10^{-4}\ M^{0.713} \text{ from toluene results}$$
$$= 1.39 \times 10^{-4}\ M^{0.714} \text{ from butanone results}$$

This value of the exponent is appreciably higher than that of equation (7), and lines on Fig. 3 corresponding to these equations cross that of equation (7) at a small angle. Nevertheless, the deviations are small.

It seems legitimate to conclude that, both for fractions and for completely unfractionated polystyrenes, the constants of the Mark-Houwink equations remain unaltered over the wide molecular range 1,000–2,000,000, and that within a fairly large experimental error, their magnitudes are given by equations (7) and (6) respectively.

SUMMARY.

Intrinsic viscosities in benzene at 25°C. and cryoscopic molecular weights have been measured for series of unfractionated and fractionated polystyrenes of molecular weight 1,000–10,000. Even for such low molecular weights the simple Staudinger relation is not applicable. Comparison of the results with recent measurements in higher molecular weight regions, suggests that the following Mark-Houwink relations hold over the molecular weight range 1,000–2,000,000 :—

For unfractionated radical polymers $[\eta] = 4.37 \times 10^{-4}\ M^{0.66}$.

For fractions $[\eta] = 2.7 \times 10^{-4}\ M^{0.66}$.

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